



## SPECIFICATION

Copolymers of *n*-vinylpyrrolidone and a vinyl, allyl or methallyl ester of an  $\alpha$ - or  $\beta$ -cyclic carboxylic acid, and their use in cosmetics

5 The present invention relates to copolymers of *N*-vinylpyrrolidone and a vinyl, allyl or methallyl ester of an  $\alpha$ - or  $\beta$ -cyclic carboxylic acid; these copolymers can be used in cosmetics, in particular in lacquers and wavesetting lotions.

10 Polyvinylpyrrolidone (PVP), which forms a film which is both elastic and strong, has been widely used in cosmetic formulations such as lacquers and wavesetting lotions.

15 However, the use of polyvinylpyrrolidone has only proved totally satisfactory when the atmospheric humidity is relatively low. In fact, polyvinylpyrrolidone possesses a certain hygroscopicity, such that, after a certain time in a humid atmosphere, the polyvinylpyrrolidone film tends to become sticky. To overcome the hygroscopicity of polyvinylpyrrolidone, it has been

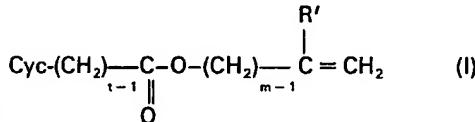
15 proposed to use copolymers of *N*-vinyl-pyrrolidone and vinyl acetate. These copolymers are less sensitive to atmospheric humidity and furthermore possess good fixing properties. By varying the proportion of vinyl acetate, it is possible to influence some of the properties of the film, in particular the hardness and the hygroscopicity.

20 However, these copolymers of *N*-vinylpyrrolidone and vinyl acetate do not always possess a very good lacquering ability and can be relatively brittle.

25 The present invention is intended to overcome the disadvantages of the films produced from *N*-vinylpyrrolidone, by providing copolymers obtained by polymerising *N*-vinylpyrrolidone with at least one vinyl, allyl or methallyl ester of an  $\alpha$ - or  $\beta$ -cyclic carboxylic acid. In fact, it has been found that by polymerising *N*-vinylpyrrolidone with this type of ester, the copolymers obtained possess excellent properties, in particular cosmetic properties, that is to say moderate hardness, 25 very low hygroscopicity, good lacquering ability and a pleasant feel.

The present invention provides polymers which contain units resulting from the polymerisation of (a) *N*-vinylpyrrolidone with (b) at least one vinyl, allyl or methallyl ester of an  $\alpha$ - or  $\beta$ -cyclic carboxylic acid, corresponding to the following formula:

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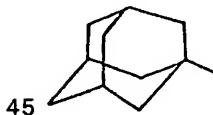


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in which  $\text{R}'$  represents a hydrogen atom or a methyl radical,  $m$  is 1 or 2 and  $t$  is 1 or 2; such that if  $t = 1$ , Cyc represents a monocyclic or polycyclic, saturated or unsaturated radical such as:

(i) a radical of the formula:

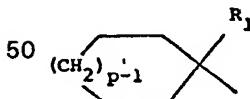
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(ii) a radical of the formula:

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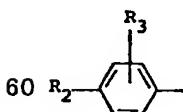
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in which  $\text{R}_1$  represents a hydrogen atom or a methyl radical and  $p$  is 1 or 2,

55 (iii) a radical of the formula:

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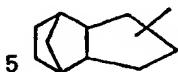
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in which  $\text{R}_2$  represents a hydrogen atom or a methyl, ethyl, tert.-butyl, ethoxy, butoxy or dodecoxy radical and  $\text{R}_3$  represents a hydrogen atom, an alkyl radical having 1 to 4 carbon

65 atoms or an alkoxy radical having 1 to 4 carbon atoms, or

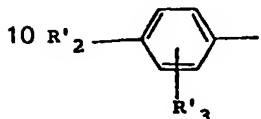
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(iv) a radical of the formula:



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and if  $t = 2$ , Cyc represents a radical of the formula:



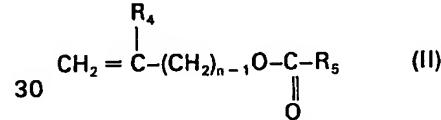
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15 15 in which  $R'2$  and  $R'3$  are as defined under  $R_2$  and  $R_3$ , respectively.

Amongst the vinyl, allyl and methallyl esters of the formula (I), the following may be mentioned in particular: the vinyl, allyl and methallyl esters of adamantane-1-carboxylic acid, cyclohexane-carboxylic acid, cyclopentane-carboxylic acid, benzoic acid, phenylacetic acid, 4-tert.-butylbenzoic acid, 1-methylcyclopentane-1-carboxylic acid, 1-methylcyclohexane-1-carboxylic acid, tricyclo[5.2.1.0<sup>2,6</sup>]decane-3-carboxylic acid and tricyclo[5.2.1.0<sup>2,6</sup>]decane-4-carboxylic acid, these last two acids being sold, in the form of a mixture, by HOECHST, under the tradename TCD Carboxylic Acid S.

The copolymers according to the invention can also contain units of at least one other monomer which is:

25 25 1. A vinyl, allyl or methallyl ester of the formula:



30

in which  $n$  is 1 or 2,  $\text{R}_4$  represents a hydrogen atom or a methyl radical and  $\text{R}_5$  represents a linear or branched alkyl radical having from 1 to 21 carbon atoms.

35 35 Amongst the esters of the formula (II), the following may be mentioned in particular: the vinyl, allyl and methallyl esters of acetic acid, propionic acid, butyric acid, pivalic acid, hexanoic acid, octanoic acid, decanoic acid, lauric acid, myristic acid, palmitic acid, stearic acid, isostearic acid, behenic acid, 2-ethyl-hexanoic acid, 2,2-dimethylpentanoic acid, 2,2-dimethyl-hexanoic acid, 2,2-dimethyloctanoic acid, 2,2-dimethyl-decanoic acid, 2,2,4,4-tetramethylvaleric acid, 40 isopropyl-2,3-dimethylbutyric acid, 2-methyl-2-ethylheptanoic acid, 2-methyl-2-propylhexanoic acid, 2-methyl-2-isopropylhexanoic acid, 3,5,5-trimethylhexanoic acid and their isomers, and also mixtures thereof and in particular the mixture sold by SHELL under the tradename "Versatic Acid" and the mixtures sold by UGINE-KUHLMANN under the tradenames "CEKANOIC C<sub>8</sub>, C<sub>9</sub> and C<sub>10</sub> Acids".

45 45 2. A vinyl ether of the formula:



45

in which  $\text{R}_6$  represents a linear or branched alkyl radical having from 6 to 18 carbon atoms.

50 50 Amongst the vinyl ethers of the formula III, the following may be mentioned: hexyl vinyl ether, octyl vinyl ether, decyl vinyl ether, dodecyl vinyl ether, hexadecyl vinyl ether and octadecyl vinyl ether.

3. An  $\alpha$ -olefine of the formula:

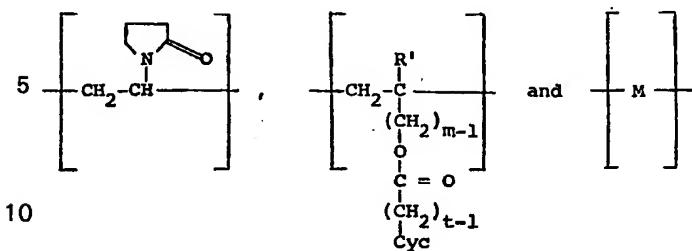


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in which  $s$  is an integer from 3 to 15.

Amongst the  $\alpha$ -olefines of the formula IV, the following may be mentioned: hex-1-ene, oct-1-ene, dec-1-ene, dodec-1-ene and octadec-1-ene.

60 60 The copolymers according to the invention can generally be represented as having recurring units of the following general formula:



15 in the relative amounts, x, y and z respectively, in which Cyc, R', m and t are as defined above, M is a unit derived from at least one monomer as represented by the formulae (II) to (IV) above, x represents from 20 to 90%, and preferably from 25 to 80%, by weight, y represents from 1 to 70%, and preferably from 10 to 50%, by weight, and z represents from 0 to 70%, and preferably from 10 to 60% by weight.

However, it is important to note that the sum of the non-homopolymerisable monomers should not exceed 50 mol% of the total of the monomers. The non-homopolymerisable monomers according to the invention are:

(i) the compounds of the formula (I) when  $m = 2$ .

(i) the compounds of the formula (I) when  $m = 2$ ,  
 (ii) the compounds of the formula (II) when  $n = 2$ , and  
 (iii) the compounds of the formulae (III) and (IV).

Preferably, when  $m = 2$  in the monomers of the formula (I), the mol percentages for  $x$ ,  $y$  and  $z$  are as follows:  $x$  represents from 50 to 90%,  $y$  represents from 10 to 50% and  $z$  represents from 0 to 40%.

The copolymers according to the invention, as defined above, generally have an average molecular weight from 5,000 to 60,000 and more particularly from 10,000 to 45,000, these molecular weights being number-average molecular weights determined by osmometry.

30 The present invention also provides a process for the preparation of the copolymers. They can 30 be prepared by the conventional methods of polymerisation, that is to say either in solution in a solvent, or in bulk, or also in suspension in an inert liquid, or in emulsion.

The polymerisation reaction can also be carried out in suspension in water saturated with sodium chloride, in the presence of a protective colloid or suspending agent, such as polyvinyl alcohol, cross-linked polyacrylic acid or the product known under the tradename Cellosolve WP-09; this makes it possible to obtain the polymer in the form of beads at the end of the reaction.

The polymerisation initiators which can be used in the polymerisation process are preferably azo-bis-iso-butyronitrile, peresters, percarbonates or oxidation/reduction systems, these initiators being used either singly or as a mixture.

The polymerisation reaction is preferably carried out at a temperature from 45 to 100°C and

more particularly at the reflux temperature of the reaction mixture.

The reaction time is preferably from 6 to 24 hours. The present invention is not limited to the use of the above-mentioned solvents.

The present invention also provides a cosmetic composition which contains at least one copolymer according to the invention as a resin, these compositions being presented in the form of wavestetting lotions, aerosol lacquers, rinses or shampoos.

According to the invention, the cosmetic compositions generally contain from 0.5 to 10% by weight of at least one copolymer of this invention.

The wavesetting lotions according to the invention are usually in the form of aqueous

The alcohols which are generally used for producing these wettability solutions are preferably

55 The aerosol hair lacquers according to the invention can be obtained by dissolving in an  
low molecular weight lower aliphatic alcohols such as ethanol or isopropanol.

alcohol, at least one copolymer of this invention, this solution being placed in a pressurised or

According to this embodiment, the copolymer is preferably used in an amount from 0.7 to 50 % by weight.

The aerosol lacquers can also contain an auxiliary solvent which is suitably present in an amount from 2 to 25% by weight.

Amongst these auxiliary solvents, the following may be mentioned in particular; methylene chloride, trichloroethane, ethyl chloride, acetone, ethyl acetate and dichlorodifluoromethane.

In the aerosol lacquers according to the invention, the alcohol which can be either ethanol or 65

isopropanol, is generally present in an amount of 5 to 80%, and preferably 6 to 70%, by weight.

Propellants which can be used in particular for the aerosol lacquers are fluorochlorinated hydrocarbons, either used singly or as a mixture, especially those known under the tradenames 5 "Freon" and in particular "Freons 11, 12, 22, 133A and 142b".

Propellants which can also be used are carbon dioxide, nitrous oxide ( $N_2O$ ), dimethyl ether and hydrocarbons such as propane, butane and isobutane, these propellants being used either singly or as a mixture with one another or with one or more "Freons".

When the compositions are in the form of shampoos, they contain, in addition to the polymer 10 according to the invention, at least one anionic, cationic or non-ionic surface-active agent.

The compositions according to the invention can also contain various ingredients which are generally used in this type of composition, such as plasticisers, agents for imparting gloss, perfumes, dyestuffs and restructuring agents.

The following examples further illustrate the present invention:—

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#### PREPARATION EXAMPLES

##### EXAMPLE 1

A solution of 35 g of vinyl 4-tert.-butyl-benzoate, 35 g of vinyl acetate, 30 g of N-vinylpyrrolidone and 0.2 g of azo-bis-isobutyronitrile in 300 g of ethanol is introduced into a 20 round-bottomed flask equipped with a condenser, a mechanical stirrer and a nitrogen inlet.

The mixture is subsequently heated under reflux for 24 hours, whilst stirring, and the polymer is then precipitated in ethyl ether. After filtration, the polymer is dried at 50°C under reduced pressure.

The yield is 42% and the polymer obtained has a viscosity of 1.56 cP, measured in a 5% 25 strength solution in dimethylformamide (DMF) at 34.6°C.

##### EXAMPLE 2

30 g of N-vinylpyrrolidone, 15 g of vinyl cyclohexanoate, 55 g of vinyl acetate, 0.5 g of tert.-butyl 2-ethylhexanoate and 25 g of ethanol are introduced into a round-bottomed flask 30 equipped with a condenser, a mechanical stirrer and a nitrogen inlet.

The mixture is subsequently heated under reflux for 24 hours, whilst stirring, and then, when the polymerisation reaction is complete, the polymer is precipitated in ethyl ether.

After filtration, the polymer is dried at 50°C under reduced pressure.

The yield is 80% and the polymer obtained has a viscosity of 2.4 cP, measured in a 5% 35 strength solution in dimethylformamide (DMF) at 34.6°C.

The copolymers in Table I were also prepared in accordance with the procedures described in Example 1 and 2 above:

TABLE 1

Monomer % by weight	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9	Example 10	Example 11	Example 12	Example 13	Example 14
N-vinylpyrrolidone	70	50	30	70	50	40	30	35	40	40	30	35
vinyl 4-tert.-butylbenzoate	30	50	70	15	25	10	15	15	5	5	15	12
allyl 4-tert.-butylbenzoate												
vinyl benzoate												
vinyl cyclopentanoate												
vinyl phenylacetate												
allyl benzoate												
vinyl acetate												
vinyl propionate												
allyl propionate												
allyl stearate												
octadecyl vinyl ether												
dodecyl vinyl ether												
Yield %	80	62	26	73.2	70	40	42	55	48	59	92	64
Viscosity (5% strength solution in DMF at 34.6°C)	2.05	1.89	1.67	1.88	1.54	1.52	1.82	1.69	1.54	1.68	2.3	1.73

\*obtained in accordance with the process of Example 1

\*\*obtained in accordance with the process of Example 2

**COMPOSITION EXAMPLES****EXAMPLE A**

An aerosol lacquer is prepared according to the invention by packaging the following ingredients in a container:

5	Copolymer prepared in accordance with Example 1	3 g	5
	Ethanol (or isopropanol)	40 g	
	Methylene chloride	20 g	
	Propellant: mixture of 35% of propane and		
10	65% of butane	40 g	10

In this example, the copolymer prepared in accordance with Example 1 can be replaced by the same amount of the copolymer prepared in accordance with Example 4.

15	<b>EXAMPLE B</b>		15
	An aerosol lacquer is prepared according to the invention by mixing the following ingredients:		

	Copolymer prepared in accordance with Example 3	3 g	
	Ethanol	60 g	
20	Propellant: mixture of 35% of propane and		20
	65% of butane	40 g	

**EXAMPLE C**

25	An aerosol lacquer is prepared according to the invention by mixing the following ingredients:		25
	Copolymer prepared in accordance with Example 2		

	Ethanol q.s.p.	7.6 g	
		100 g	

30	22 g of the composition thus obtained are then packaged in an aerosol container together with 78 g of a 61.5/38.5 mixture of Freon 11 and Freon 12.		30
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When this lacquer is applied to the hair, no powder formation is observed with time and the hair does not become sticky, even in a humid atmosphere.

35	<b>EXAMPLE D</b>		35
	A wavesetting lotion is prepared according to the invention by mixing the following ingredients:		

40	Polymer prepared in accordance with Example 4	2 g	
	Perfume	0.15 g	
	Ethanol	46 g	40
	Water q.s.p.	100 g	

45	In this example, the polymer prepared in accordance with Example 4 can advantageously be replaced by the same amount of one of the polymers prepared in accordance with Examples 5 to 8 or 14.		45
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After this wavesetting lotion has been applied to the hair, the latter is wound onto wavesetting rollers and then dried. The waveset holds very well with time and there is no powder formation.

50	<b>EXAMPLE E</b>		50
	A wavesetting lotion is prepared according to the invention by mixing the following ingredients:		

55	Copolymer prepared in accordance with Example 9	3.5 g	
	Perfume	0.2 g	
	Sufficient dyestuff to colour the lotion	0.15 g	55
	Isopropyl alcohol	50 g	
	Water q.s.p.	100 g	

60	When applied in the conventional manner, this wave setting lotion makes it possible to impart, to the hair, a glossy appearance and an excellent hold with time.		60
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In this example, the polymer prepared in accordance with Example 9 can advantageously be replaced by the same amount of one of the polymers prepared in accordance with Examples 10 to 12.

65	<b>EXAMPLE F</b>		65
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A rinsing product or "rinse", in the form of an emulsion, is prepared according to the invention by mixing the following ingredients:

Liquid petrolatum	9.6 g	
5 Polyglycerolated fatty alcohols ( $C_{16}C_{18}$ ) (containing 2 to 6 mols of glycerol)	6.5 g	5
Polymer prepared in accordance with Example 13	1.5 g	
Water q.s.p.	100 g	

10 This product is applied to hair which has been washed and towel-dried, by spreading it carefully over the whole head of hair. After a few minutes have elapsed, the hair is carefully rinsed.

The hair is glossy and easy to comb out.

In this example, the polymer according to Example 13 can advantageously be replaced by the 15 same amount of one of the polymers prepared in accordance with Examples 2 to 5 and 8. 15

**EXAMPLE G**

An ionic shampoo is prepared according to the invention by mixing the following ingredients:

20 Triethanolamine lauryl-/myristyl-sulphate	12 g	20
Copra diethanolamide	2 g	
Myristyldimethylamine oxide	1.5 g	
Copolymer prepared in accordance with Example 10	1.5 g	
Lactic acid q.s.p. pH = 6.5		
25 Water q.s.p.	100 g	25

**EXAMPLE H**

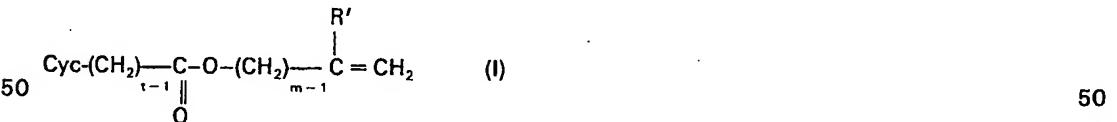
A cationic shampoo is prepared according to the invention by mixing the following ingredients:

30 Cetyltrimethylammonium bromide	2 g	30
Polyglycerolated lauryl alcohol containing 4 mols of glycerol	12 g	
Polymer prepared in accordance with Example 6	1 g	
35 Perfume	0.2 g	35
Lactic acid q.s.p. pH = 4.5		
Water q.s.p.	100 g	

In this example, the polymer prepared in accordance with Example 6 can advantageously be 40 replaced by the same amount of one of the polymers prepared in accordance with Examples 7 or 13. 40

**CLAIMS**

1. A copolymer derivable from the polymerisation of (a) N-vinylpyrrolidone and (b) at least 45 one vinyl, allyl or methallyl ester of an  $\alpha$ - or  $\beta$ -cyclic carboxylic acid of the formula:

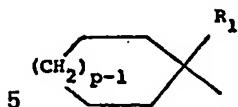


in which  $\text{R}'$  represents a hydrogen atom or a methyl radical,  $m$  is 1 or 2 and  $t$  is 1 or 2 such that if  $t = 1$ , Cyc represents:

55 (i) a radical of the formula:

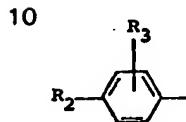


(ii) a radical of the formula:



5

in which R<sub>1</sub> represents a hydrogen atom or a methyl radical and p is 1 or 2,  
 (iii) a radical of the formula:



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in which R<sub>2</sub> represents a hydrogen atom or a methyl, ethyl, tert.-butyl, ethoxy, butoxy or dodecoxy radical and R<sub>3</sub> represents a hydrogen atom, an alkyl radical having 1 to 4 carbon atoms or an alkoxy radical having 1 to 4 carbon atoms, or  
 (iv) a radical of the formula:

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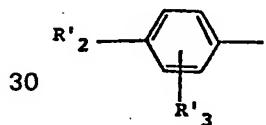
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25 and if t = 2, Cyc represents a radical of the formula:

25



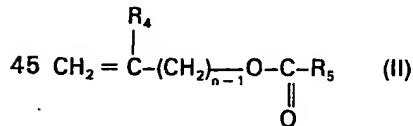
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in which R'<sub>2</sub> and R'<sub>3</sub> are as defined under R<sub>2</sub> and R<sub>3</sub> respectively.

2. A copolymer according to claim 1, in which the said ester is a vinyl, allyl or methallyl ester of adamantan-1-carboxylic acid, cyclohexanecarboxylic acid, cyclopentane-carboxylic acid, 35 benzoic acid, phenylacetic acid, 4-tert.-butylbenzoic acid, 1-methylcyclopentane-1-carboxylic acid, 1-methylcyclohexane-1-carboxylic acid, tricyclo[5.2.1.0<sup>2,6</sup>]decane-3-carboxylic acid or tricyclo[5.2.1.0<sup>2,6</sup>]decane-4-carboxylic acid.

3. A copolymer according to Claim 1 or 2 which is also derivable from at least one other 40 monomer which is:

(i) a vinyl, allyl or methallyl ester of the formula:



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in which n is 1 or 2, R<sub>4</sub> represents a hydrogen atom or a methyl radical and R<sub>5</sub> represents a 50 linear or branched alkyl radical having from 1 to 21 carbon atoms,

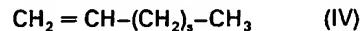
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(ii) a vinyl ether of the formula:



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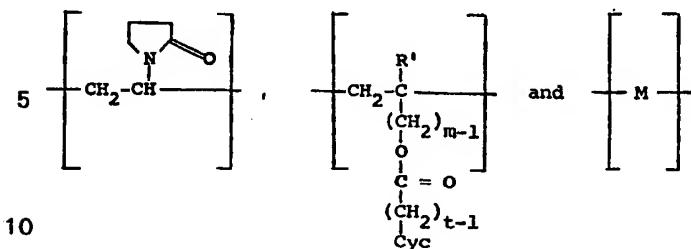
55 in which R<sub>6</sub> represents a linear or branched alkyl radical having from 6 to 18 carbon atoms, or  
 (iii) an  $\alpha$ -olefine of the formula:



60 in which s is an integer from 3 to 15.

60

4. A copolymer according to any one of the preceding claims, which comprises units of the following formulae



15 in the relative amounts x, y and z, respectively, in which Cyc, R', m and t are as defined in  
Claim 1, M is a unit derived from at least one monomer of formula (II), (III) or (IV) as defined in  
Claim 3, x represents from 20 to 90% by weight, y represents from 1 to 70% by weight, and z  
represents from 0 to 70% by weight.

5. A copolymer according to Claim 4, in which x represents 25 to 80% by weight, y represents 10 to 50% by weight and z represents 10 to 60% by weight.

6. A copolymer according to any one of the preceding claims, which has a number-average molecular weight, determined by osmometry, of 5,000 to 60,000 and preferably between 10,000 and 45,000.

7. A copolymer according to Claim 6 in which the said molecular weight is 10,000 to 45,000.

8. A copolymer according to Claim 1 specifically identified herein.

25 9. Process for the preparation of a copolymer as claimed in any one of Claims 1 to 8 which comprises polymerising the constituent monomers, in solution, in bulk or in suspension, in the presence of a polymerisation initiator in an amount of 0.1 to 6% by weight based on the total weight of the monomers.

10. Process according to Claim 9 in which the polymerisation is carried out in suspension in water, in the presence of a protective colloid, the polymerisation initiator being azo-bis-30 isobutyronitrile.

11. Process according to Claim 9 or 10, in which the polymerisation is carried out at a temperature of 45 to 100°C for 6 to 24 hours.

12. Process according to Claim 9 substantially as described in Example 1 or 2 or part thereof.

35 13. A copolymer according to claim 1 whenever prepared by a process as claimed in any one of claims 9 to 12.

14. A composition suitable for use in cosmetics which comprises, in a suitable vehicle, at least one copolymer as claimed in any one of Claims 1 to 8 and 13.

15. A composition according to Claim 14 which contains from 0.5 to 10% by weight of 40 copolymer.

16. A composition according to Claim 14 or 15 which is in the form of an aqueous or aqueous-alcoholic solution, the copolymer concentration being from 1 to 3% by weight.

17. A composition according to claim 14 or 15 which is in the form of a solution in an alcohol mixed with a propellant, and is packaged in an aerosol container, the copolymer

18. A composition according to Claim 16 or 17 in which the alcohol is ethanol or

19. A composition according to Claim 17 or 18 which contains an auxiliary solvent in an amount of 2 to 25% by weight.

amount of 3 to 35% by weight, based on the total weight of the composition.

20. A composition according to Claim 14 or 15 which contains an anionic, cationic or non-ionic surface-active agent.

21. A composition according to any one of Claims 14 to 20 which contains at least one of a plasticiser, agent for imparting gloss, perfume, dyestuff or restructuring agent.

22. A composition according to Claim 14 substantially as described in any one of Examples 55 A to H.

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